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(57) Abstract

A method of fabricating dielectric–coated metal flakes is provided, using multiple release coatings on a flexible web to separate a stack of coated metal layers. The method involves forming a release layer on the web material, then forming a dielectric coated metal layer on the release layer. The dielectric coated metal layer includes a lower dielectric layer, a layer of a reflective metal, and an upper dielectric layer. On top of the upper dielectric layer of the coated metal layer, another release layer is formed, and the process repeated to form a "stack" of dielectric–coated metal layers on a single film layer, each such layer separated from each other and from the web material by release layers. The coated metal layers are separated from each other by dissolving the release layers, and can then be fragmented to produce thin metal flakes. The present invention also provides very thin metal flakes having substantial rigidity and resistance to environmental attack. The flakes have a thin aluminum reflector layer coated on both sides by thin silicon monoxide dielectric layers.

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BRIGHT ALUMINUM PIGMENT

BACKGROUND OF THE INVENTION

1. The Field of the Invention

The present invention relates generally to metal flake pigments and methods for making such pigments. More specifically, the present invention relates to metal flake pigments having improved reflective properties, and improved methods for their manufacture.

2. The Relevant Technology

Pigments are generally used to contribute to the optical and other properties of applications such as coatings, inks, extrusions, paints, finishes, glass, ceramics and cosmetics. Many varieties of pigments exist, some of which are based on metal flakes. These metal flakes include a thin film metal layer for improving the luster, sparkle, shine, absorption, hiding and/ or reflective properties of the pigments. The optical performance of the pigment is ultimately constrained by the optical properties of its constituent metal flakes.

In general, it is known that to achieve the greatest specular reflectance across visible wavelengths, metal flakes should individually lay as flat as possible on the surface to which the pigment is applied. In a collection of numerous flakes, the greatest reflectance, and hence greatest optical brightness, occurs when the flakes are uniformly flat and approximately co-planar, thereby oriented to expose the greatest amount of surface area of the metal flakes to the incident light and reflect as much of that light as possible.

A major factor affecting reflectance characteristics is the size or dimensions of the flake as the flake is used in a particular application. For example, if the flakes are relatively thick, a plurality of these thick flakes combined together in an application are prevented from lying together in a generally flat or horizontal singular plane because adjacent flakes cannot easily overlap each other due to their thickness. As a result, many flakes are adversely

caused to be oriented in a substantially vertical manner, and the plurality of flakes are formed into a radically non-planar layer. Incident light then exposed upon the non-planar layer is subject to extreme scatter and non-specular reflection. Thus, the favorable reflective properties of the application are diminished by the presence of thick flakes. In addition, thick flakes frequently cause other difficulties, such as the clogging of automatic-spray paint guns during painting applications.

Given the disadvantages of thick flakes, it would be advantageous to provide very thin metal flakes. Typical metal flakes are multi-layered structures having a central metal layer and one or more coating layers to improve various flake properties. Although the coating layers provide additional rigidity and favorable optical properties to the metal flake, the use of coating layers increases the flake thickness. Alternatively, the metal flakes can be uncoated metal. However, uncoated metal is subject to environmental degradation, such as corrosion of the reactive metal surface, or physical abrasion. In addition, as the thicknesses of the flakes decreases, their rigidity also decreases and they begin to curl and/ or wrinkle. This lack of sufficient rigidity decreases favorable planarity and reflective properties because incident light exposed upon the flakes is subject to scatter and non-specular reflection. When applied onto a surface in application, such thin flakes will assume the microscopic defects in the contour of that surface. For example, if the microscopic contour is rough, the flakes will be oriented in a rough or non-planar fashion. Again, degraded reflective properties result because incident light exposed to the surface is subject to increased scatter and non-specular reflection.

Various attempts have been made to provide metal flakes having improved properties. For example, U.S. Patent No. 5,198,042, entitled "Aluminum Alloy Powders for Coating Materials and Materials Containing the Alloy Powders," teaches alloying the metal flake

with other materials and metals to reduce the adverse curling, wrinkling and malleability of thin flakes. Alloying, however, dilutes the reflectance properties of the flake.

U.S. Patent No. 3,622,473, entitled "Method of Providing Aluminum Surfaces with Coatings," teaches increasing flake rigidity by oxidizing the reflector of the flake to form a rigid, outer oxide layer. This oxidation reportedly increases flake rigidity. Disadvantageously, such oxide layers have poor reflective properties, so that whenever an oxide is used, the inherent reflectance properties of the flake are decreased. Additionally, oxides are typically formed at defect sites on the flakes which then tend to prevent a uniform application across the surface of the flake. This non-uniformity causes a further reduction in reflectance and can also cause a mottled applicational appearance.

In U.S. Patent No. 4,213,886, entitled "Treatment of Aluminum Flake to Improve Appearance of Coating Compositions," a surface bound species that pulls the flake flat in a coating resin is disclosed. This method, however, requires chemical tailoring of the flake and the resin in order achieve chemical compatibility. Such compatibility is difficult and thus far has not proved to be practical.

In U.S. Patent No. 4,629,512, entitled "Leafing Aluminum Pigments of Improved Quality," flakes are floated on a resin coating. Adversely, this method submits the flake to durability attacks because the flake is unprotected. Such attacks primarily include corrosion, which not only corrodes the flake but tends to give the application a mottled or discolored appearance. Additionally, if this method were used in conjunction with another resinous application, such as a clear overcoat paint, the overcoat itself would tend to disfavorably disrupt the planar orientation of the flake because of solvent penetration. Again, reflectance properties are decreased.

U.S. Patent No. 5,593,773, entitled "Metal Powder Pigment," discloses pre-cracked flakes having such a small aspect ratio that malformation of the flake is essentially

impossible. A shrinking aspect ratio, however, also correspondingly shrinks the inherent reflectance capability of the flake. This is so because as the aspect ratio becomes smaller, any non-planar flake orientation during applicational use exposes such a small surface area of the flake to the incident light that reflection of that light is minimal. Other prior art proposals, such as encapsulating a metal flake in a metallic coating, also decrease the flake aspect ratio and reflectivity, which adversely eliminates the ability of the flake to reflect incident light.

Other approaches attempt to improve flake rigidity by applying single or multiple layer coatings on the flake surfaces. Thus far, the single layer coatings have been so thick that reflective properties are detrimentally reduced, since the coatings greatly increase scattering losses. Prior art multiple layer coatings induce even more scatter and adversely cause light to diffuse at the boundaries between various layers. In addition, coatings thus far have essentially been organic, and inherent within the crystalline structure of these organic coatings is a natural limitation as to how thinly the coatings can be applied and still provide additional rigidity or environmental protection. Disadvantageously, the minimum thickness is still so large that other applicational processes remain burdened by this thickness. Such processes include spraying the flakes through an automatic-spray paint gun. Moreover, organic coatings when applicationally used in a solvent eventually lose structural rigidity because of dissolution-related effects.

Other efforts have focussed on replacing the metal layer with a multi-layered structure that does not use metals at all. For example, U.S. Patent No. 4,309,075, entitled "Multilayer Mirror with Maximum Reflectance," teaches multiple layer coatings that merely simulate a metal flake and its reflective properties. These coatings, known as "high-low" coatings because of their alternating layers of high and low indices of refraction, are used to create a reflector that simulates the reflective properties of a metal flake. Another example is

described in U.S. Patent No. 3,123,490 issued to Bolomey, in which a layer of zinc sulfide is coated on both surfaces with magnesium fluoride. Although these structures offer some advantages, the flakes are typically very thick (about 215 nm) and cannot be used in many applications requiring thin flakes. Moreover, it is often necessary to have numerous layers of alternating high-low coatings to simulate the reflectance of a metal flake. But, as the number of layers and the flake thickness increases, manufacturing complexities and economic burdens increase as well.

One convenient method of manufacturing thin metal flakes is to deposit the flake materials on a web of flexible material that can be used in a roll coater apparatus, using conventional physical vapor deposition (PVD) processes. The film thus formed is removed from the web and fractured, to produce metal flakes, which can then be further processed as desired. These conventional methods suffer from several disadvantages. In order to provide a means for releasing the metal film from the flexible web, the web must first be coated with a material that will adhere to both the web and the deposited material, but which can later be removed by dissolving in an appropriate solvent. Typical release coatings are organic in nature, and require the use of organic solvents for dissolution. The use of organic solvents, however, increases costs, and presents additional problems of organic chemical wastes and safety issues. Moreover, although it would be desirable to carry out all the coating processes by PVD in vacuum, materials typically used for organic release layers are not suitable for such processes. Thus, for example, U.S. Patent No. 3,949,139 to Dunning et al., entitled "Laminar Reflective Platelets and Compositions and Articles Comprising Them," discloses a process using organic release coatings of materials such as waxes. The flexible web is coated with the wax by a gravure printing technique, but such a process can not be done inside a PVD vacuum chamber.

Several known processes use inorganic salt layers such as sodium fluoride or sodium tetraborate as the release layer. These sodium salts are water soluble, eliminating the need for organic solvents. For example, U.S. Patent No. 4,879,140 to Gray et al., entitled "Method for Making Pigment Flakes," discloses a plasma deposition process using a release layer of Teflon® or alternatively sodium tetraborate. When the release layer is formed of sodium tetraborate, the layer can be dissolved in water to release a deposited film from a Pyrex or quartz substrate. U.S. Patent No. 4,168, 986 to Venis, Jr., entitled "Method for Preparing Lamellar Pigments," discloses a vacuum deposition process using a sodium fluoride release layer deposited on a polyester web. A multi-layer structure of titania and zirconia dielectrics is then deposited on the release layer, and the release layer dissolved.

These prior art processes, however, are inefficient, since the web substrate must be coated with a release layer and a deposited film, then released from the film before it can be coated again. Thus, the loading capacity of the web is limited, resulting in equipment under-utilization and higher costs.

Accordingly, there is a need for metal flakes which are very thin and have good reflectance properties, but have more rigidity than uncoated metal flakes, and resistance to environmental degradation. Additionally, there is a need for methods of inexpensively and efficiently producing such thin metal flakes.

SUMMARY

In accordance with the invention as embodied and broadly described herein, the foregoing is achieved by providing a method of fabricating a plurality of dielectric-coated metal flakes. The method uses multiple release coatings on a flexible web to separate a stack of coated metal layers. The method involves forming a release layer on the web material, then forming a dielectric coated metal layer on the release layer. The dielectric coated metal layer includes a lower dielectric layer, a layer of a reflective metal, and an upper dielectric

layer. On top of the upper dielectric layer of the coated metal layer, another release layer is formed, and the process repeated to form a "stack" of two dielectric-coated metal layers on a single film layer, separated from each other and from the web material by release layers. The process can further be repeated to form several stacked and separated dielectric-coated metal layers. When the desired number of stacked coated metal layers have been formed, the coated metal layers are separated from each other and from the web by dissolving the release layers. The coated metal layers can then be fragmented to produce thin metal flakes.

In another aspect, the present invention relates to very thin metal flakes having increased rigidity relative to uncoated flakes, and resistance to environmental attack. In this embodiment is provided a thin dielectric-coated metal flake having a bottom dielectric layer of silicon monoxide having a thickness of about 100 to about 200 Å, a reflector layer of aluminum on the bottom dielectric layer having a thickness of about 400 to about 800 Å, and a top dielectric layer of silicon monoxide on the reflector layer, to form a thin dielectric-coated metal flake. The dielectric metal flake has a thickness of from about 60 to 120 nm, a high reflectivity, and increased rigidity and durability, due to the presence of the very thin SiO layers. Such flakes can be formed by vapor deposition methods, including the multiple stack methods of the present invention.

Other objects and features of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to more fully understand the manner in which the above-recited and other advantages and objects of the invention are obtained, a more particular description of the invention will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. Understanding that these drawings depict only typical

embodiments of the invention and are not therefore to be considered limiting of its scope, the invention in its presently understood best mode for making and using the same will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

Figure 1 is a schematic cross-section of a dielectric-coated metal layer of the present invention.

Figure 2 is a schematic cross-section of a dielectric-coated metal layer of the present invention on a flexible web material.

Figure 3 is a schematic cross-section of a stack of six dielectric-coated metal layers of the present invention on a flexible web material.

Figure 4 is a schematic cross-section of a dielectric-coated metal flake of the present invention.

Figure 5 is a graph showing reflectance as a function of wavelength for uncoated aluminum and for dielectric coated metal flakes of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In one aspect, the present invention is directed to a method of fabricating dielectric-coated metal flakes. Referring to Fig. 1, a dielectric coated metal layer 10 is shown. The dielectric-coated metal layer 10 is composed of a bottom dielectric layer 12, a reflector layer 14, and a top dielectric layer 16. Referring to Fig. 2, the method involves forming a release layer 18 on a web material 20, and a plurality of dielectric coated metal layers 10 stacked on release layer 18 and separated by additional release layers (shown in Fig. 3). The coated metal layers are separated from each other and from the web by dissolving release layers 18 in a suitable solvent, then are fragmented to produce thin dielectric-coated metal flakes. The layers of the present invention can be formed by any conventional deposition technique. A

preferred deposition technique is physical vapor deposition (PVD), and for convenience, the invention will be described herein with reference to the PVD process.

Referring now to Figure 3, in a first step, release layer 18 is formed on web material 20. The web material 20 can be any material suitable for use in a roll coating apparatus and compatible with PVD processing. Suitable web materials such as metals and polymers are known in the art. A preferred web material is polyester.

The release layer 18 is composed of a material that is capable of adhering to web material 20 and to subsequently deposited bottom dielectric layer 12 sufficiently to hold layer 12 in place during vacuum processing, but which can be easily dissolved in post-processing. Preferably, release layer 18 is an inorganic material that can be deposited onto web material 20 in a PVD vacuum chamber, thus eliminating the need to separately coat the web material before introducing the web to the PVD apparatus. Suitable release layer 18 materials include inorganic salts which are soluble in aqueous solution at room temperature or moderately elevated temperatures convenient for processing. Examples of suitable release layer 18 materials include NaCl, NaI, $Na_5Al_3F_{14}$, Na_3AlF_6, and $Na_2B_4O_7$. A preferred release layer 18 material is disodium tetraborate, $Na_2B_4O_7$. The release layer 18 can be deposited to any convenient thickness, preferably a thickness of about 150 to about 500 Å, more preferably about 150 to about 250 Å, and most preferably about 200 Å, to provide adequate adherence and convenience in post-processing steps.

In another step, bottom dielectric layer 12 is formed on release layer 18. The bottom dielectric layer 12 may be formed of any material having the desired dielectric properties, as determined according to the ultimate use of the coated metal flakes. In some applications, it is desirable to form bottom dielectric layer 12 of a low index material; *i.e.*, a material having an index of refraction of about 1.65 or less. Suitable low index materials include, for example, silicon dioxide, aluminum oxide, magnesium fluoride, aluminum fluoride, cerium

fluoride, lanthanum fluoride, neodymium fluoride, samarium fluoride, barium fluoride, calcium fluoride, lithium fluoride, and combinations of these materials.

In other applications, it is desirable to form dielectric layer 12 of a high index material; *i.e.*, a material having an index of refraction greater than about 1.65. Suitable high index materials include, for example, zinc sulfide, zinc oxide, zirconium oxide, titanium dioxide, carbon, indium oxide, indium-tin-oxide, tantalum pentoxide, cerium oxide, yttrium oxide, europium oxide, iron oxides, hafnium nitride, hafnium carbide, hafnium oxide, lanthanum oxide, magnesium oxide, neodymium oxide, praseodymium oxide, samarium oxide, antimony trioxide, silicon carbide, silicon nitride, silicon monoxide, selenium trioxide, tin oxide, tungsten trioxide, and combinations of these materials. Preferred dielectric materials include the silicon oxides, with silicon monoxide being particularly preferred.

The bottom dielectric layer is 12 deposited to a thickness sufficient to impart additional rigidity to the metal flake, but not so thick that the optical properties of metal reflector layer 14 are substantially adversely impaired. In general, suitable thickness are about 100 to about 200 Å, preferably about 125 to about 175 Å, and most preferably about 150 Å.

In another step of the method, reflector layer 14 is formed on bottom dielectric layer 12. The reflector layer 14 can be any material possessing the desired reflective properties, and is preferably a metal. Suitable metals include aluminum, copper, silver, gold, platinum, palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof. A preferred metal is aluminum. The reflector layer 14 can be deposited to a desired thickness, preferably in the range of about 400 to about 800 Å, more preferably about 400 to about 600 Å, and most preferably about 600 Å.

In another step, top dielectric layer 16 is formed on reflector layer 14. The materials and thickness of top dielectric layer 16 can be as described above for bottom dielectric layer

12. Preferably, top and bottom dielectric layers 16 and 12 are formed of the same material, and formed to approximately the same thickness. Thus, in a particularly preferred embodiment, top and bottom dielectric layers 16 and 12 are formed of silicon monoxide, at a thickness of about 150 Å.

It should be appreciated that the term "silicon monoxide" broadly describes a silicon-oxygen compound nominally having one mole of oxygen per mole of silicon. However, as is well-known in the art, "silicon monoxide" is typically a more complex material, having a range of oxygen-silicon mole ratios. Thus, as used herein, the term "silicon monoxide" indicates a compound of the formula SiO_x, where x is nominally 1, but ranges from about 1.0 to about 1.85.

The structure thus formed is dielectric-coated reflector layer 10 attached to flexible web material 20 by a layer of a release material 18. It is a particular feature of the method of the present invention that multiple dielectric-coated reflector layers 10 are stacked on a web material, each layer separated from adjacent layers by a release layer 18. Thus, in another step of the present method, another release layer 18a is formed on top dielectric layer 16, and another dielectric-coated metal layer 10a is formed on release layer 18a, to provide a stack of two dielectric-coated metal layers, 10 and 10a. The additional release layer 18a, and the dielectric-coated metal layer 10a, are formed just as described above for the first such layers 18 and 10, by depositing in turn release layer 18a, a bottom dielectric layer 12a, a reflective layer 14a, and a top dielectric layer 16a.

In the same fashion, the layering process is repeated to form third, fourth, fifth, etc., dielectric-coated metal layers, denoted 10b, 10c, 10d, etc., stacked on web material 20 and separated from each other and from web material 20 by release layers 18, 18a, 18b, etc. Preferably, the total number of stacked dielectric-coated metal layers 10 is two to about ten, more preferably about four to about eight, and most preferably about six. Figure 3 shows a

six-layer stack. For convenience, similar structures are referred to generally by the numeral of the base structure; *i.e.*, dielectric-coated metal layers 10, 10a, 10b, etc., are referred to generally as dielectric-coated metal layer 10, as the structures are essentially identical.

Once the desired number of stacked dielectric-coated metal layers 10 have been formed, the layers 10 are separated from each other and from web 20 by dissolving release layers 18. Preferably, release layers 18 are dissolved in an aqueous solution near room temperature, or at a moderately elevated temperature if desired to speed the rate of dissolution. Using the preferred inorganic salts described above, in the preferred thickness ranges, release layers 18 are readily dissolved in, for example, aqueous solutions such as water, at temperatures from about 20 °C to about 50 °C. The time necessary to dissolve release layers 18 depends upon the temperature of the aqueous solution, the thickness of the release layers, the specific material forming the release layers, and the number of such layers. As an example, using disodium tetraborate as the release layer material, at a thickness of about 200 Å, and using tap water at about 50 °C as the solvent, a stack of just one dielectric-coated metal layer 10 is released from web 20 after about ½ minute, a stack of four dielectric-coated metal layers 10 is released from web 20 and from each other in about two to about four minutes. A stack of six dielectric-coated metal layers 10 is released from web 20 and from each other in about six to about seven minutes, and a stack of ten dielectric-coated metal layers 10 is released from web 20 and from each other in about twelve to about fourteen minutes.

Referring now to Fig. 4, resulting dielectric-coated metal layers 10 are then fragmented to produce dielectric-coated metal flakes 110, having a bottom dielectric layer 112, a reflector layer 114, and a top dielectric layer 116. The fragmentation can be carried out by conventional means known in the art, such as by a sonic actuator or an impact grinder.

The dielectric-coated metal flakes 110 thus formed have particularly desirable properties. The flakes can be very thin, with a total thickness of about 600 to about 1200 Å, and preferably about 800 to about 1000 Å. The flakes have a large aspect ratio, typically about 150 to about 500, and more typically about 250. Because of thin dielectric layers 112 and 116 on either side of reflector layer 114, the flakes have better resistance to deformation than do uncoated flakes, so that they are able to maintain improved planarity in subsequent applications. The dielectric layers 112 and 116 also protect reflector layer 114 from environmental attack, such as chemical oxidation or physical abrasion. In addition, because dielectric layers 112 and 116 are very thin, the reflective properties of the metal comprising reflector layer 114 are not substantially degraded, and the flakes 110 have a reflectivity of about 80% or more in the visible range.

It should be understood that dielectric-coated metal flakes 110 can be subjected to whatever additional post-processing steps are appropriate for their ultimate intended use. Such processing steps are described, for example, in U.S. Patent No. 5,135,812, the disclosure of which is incorporated by reference herein.

Referring still to Fig. 4, in another aspect, the present invention is directed to thin dielectric coated metal flakes 110 having central reflector layer 114, and very thin dielectric layers 112 and 116 on each side. Such metal flakes 110 can be formed by conventional methods, but preferably are formed by the stacked layer method described above. In this embodiment, thin dielectric-coated metal flakes 110 have a bottom dielectric layer 112 of silicon monoxide having a thickness of about 100 to about 200 Å, a reflector layer 114 of aluminum on bottom dielectric layer 112 and having a thickness of about 400 to about 800 Å, and top dielectric layer 116 of silicon monoxide disposed on reflector layer 114 to form dielectric-coated metal flake 110. In a preferred embodiment, bottom and top dielectric layers 112 and 116 have the same thickness of about 125 to about 175 Å, more preferably

about 150 Å, and reflector layer 114 has a thickness of about 400 to 800 Å, more preferably about 600 Å. The overall thickness of flake 110 is about 600 to about 1200 Å, more preferably about 800 to about 1000 Å, and the aspect ratio is about 150 to about 500, preferably about 250.

The metal flakes of the present invention can be used in applications such as in flake-based pigments. Such flake-based pigments are useful in a variety of applications such as coating compositions, inks, extrusions, paints, electrostatic coatings, glass, ceramics and cosmetics.

Various additional thin film coating layers can be deposited on the dielectric-coated metal flakes, depending upon the desired optical performance of the pigment as it is used in an application, to form flake-based pigments. It should be noted that pigment flakes containing inorganic dielectrics can be ground to size at any stage during manufacture, whereas pigment flakes containing organic dielectrics need to be ground to final application size before the organic dielectrics are applied.

Various alternative embodiments of the flake-based pigments of the invention using the present dielectric coated metal flakes are described in detail in co-pending U.S. Application Serial Nos. 09/005,064 and 09/207,121, the disclosures of which are incorporated by reference herein.

The following examples are given to illustrate the present invention, and are not intended to limit the scope of the invention.

Example 1

Several samples of dielectric-coated metal flakes of the present invention were prepared by PVD, as described above, using disodium tetraborate as the release layer material, aluminum as the reflector layer material, and silicon monoxide as the dielectric

layer material. Metal flakes were prepared with top and bottom dielectric layers of 100, 150, 200 and 250 Å thickness.

Example 2

The spectral performance of the metal flakes of Example 1 in foil form was measured as a function of wavelength. Figure 5 is a reflectance-wavelength graph of the total reflectance as a function of wavelength. In the Figure, the curve 120 shows the reflectance of uncoated aluminum for comparison. The curves 122, 124 and 126 show the reflectances of aluminum coated with 150 Å, 200 Å and 250 Å, respectively. The reflectance curves 122, 124 and 126 have also been empirically supported by the results obtained from various other measurement devices (not shown) such as ink drawdowns, paint sprayouts and microscopy.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A method of fabricating a plurality of dielectric-coated metal flakes, comprising:

(a) forming a first release layer on an upper surface of a web material;

(b) forming a first dielectric-coated metal layer by:

(i) forming a bottom dielectric layer on the first release layer;

(ii) forming a reflector layer on the bottom dielectric layer; and

(iii) forming a top dielectric layer on the reflector layer to form a first dielectric-coated metal layer on the first release layer;

(c) forming a second release layer on an upper surface of the first dielectric-coated metal layer;

(d) forming a second dielectric-coated metal layer on the second release layer;

(e) releasing the dielectric-coated metal layers from the web material and from each other by dissolving the release layers in a solvent; and

(f) fragmenting the dielectric-coated metal layers to form a plurality of dielectric-coated metal flakes.

2. The method according to claim 1, which further comprises forming a third release layer on an upper surface of the second dielectric-coated metal layer, and forming a third dielectric-coated metal layer on the third release layer.

3. The method according to claim 1, which further comprises forming a plurality of alternating release layers and dielectric-coated metal layers, the plurality of layers and layers being disposed on the second dielectric-coated metal layer and alternating such that each additional dielectric-coated metal layer is separated from each underlying dielectric-coated metal layer by a release layer.

4. The method according to claim 1, wherein the release layers are formed of an inorganic salt capable of being dissolved in an aqueous solution at room temperature.

5. The method according to claim 1, wherein the release layers are formed of NaCl, NaI, $Na_5Al_3F_{14}$, Na_3AlF_6, or $Na_2B_4O_7$.

6. The method according to claim 1, wherein the dielectric layers are formed of a material having an index of refraction of about 1.65 or less.

7. The method according to claim 6, wherein the dielectric layers are formed of a material selected from the group consisting of silicon dioxide, aluminum oxide, magnesium fluoride, aluminum fluoride, cerium fluoride, lanthanum fluoride, neodymium fluoride, samarium fluoride, barium fluoride, calcium fluoride, lithium fluoride, and combinations thereof.

8. The method according to claim 1, wherein the dielectric layers are formed of a material having an index of refraction of greater than about 1.65.

9. The method according to claim 8, wherein the dielectric layers are formed of a material selected from the group consisting of zinc sulfide, zinc oxide, zirconium oxide, titanium dioxide, carbon, indium oxide, indium-tin-oxide, tantalum pentoxide, cerium oxide, yttrium oxide, europium oxide, iron oxides, hafnium nitride, hafnium carbide, hafnium oxide, lanthanum oxide, magnesium oxide, neodymium oxide, praseodymium oxide, samarium oxide, antimony trioxide, silicon carbide, silicon nitride, silicon monoxide, selenium trioxide, tin oxide, tungsten trioxide, and combinations thereof.

10. The method according to claim 1, wherein the reflector layers are formed of a material selected from the group consisting of aluminum, copper, silver, gold, platinum, palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof.

11. The method according to claim 1, wherein the metal flakes have an aspect ratio of about 150 to about 500.

12. The method according to claim 1, wherein the metal flakes have a thickness of about 600 to about 1200 Å.

13. The method according to claim 1, wherein the metal flakes have a thickness of about 800 to about 1000 Å.

14. The method according to claim 1, wherein each release layer has a thickness of about 150 to about 500 Å.

15. The method according to claim 1, wherein each dielectric layer has a thickness of about 100 to about 200 Å.

16. The method according to claim 1, wherein each reflector layer has a thickness of about 400 to about 800 Å.

17. The method according to claim 1, wherein the solvent is water.

18. A method of fabricating a plurality of dielectric-coated metal flakes, comprising:

(a) forming a first release layer on an upper surface of a web material;

(b) forming a first dielectric-coated metal layer by:

(i) forming a bottom dielectric layer of silicon monoxide on the first release layer;

(ii) forming a reflector layer on the bottom dielectric layer; and

(iii) forming a top dielectric layer of silicon monoxide on the reflector layer to form a first dielectric-coated metal layer on the first release layer;

(c) forming a second release layer on an upper surface of the first dielectric-coated metal layer;

(d) forming a second dielectric-coated metal layer on the second release layer;

(e) releasing the dielectric-coated metal layers from the web material and from each other by dissolving the release layers in a solvent; and

(f) fragmenting the dielectric-coated metal layers to form a plurality of dielectric-coated metal flakes.

19. The method according to claim 18, which further comprises forming a third release layer on an upper surface of the second dielectric-coated metal layer, and forming a third dielectric-coated metal layer on the third release layer.

20. The method according to claim 18, which further comprises forming a plurality of alternating release layers and dielectric-coated metal layers, the plurality of layers and layers being disposed on the second dielectric-coated metal layer and alternating such that each additional dielectric-coated metal layer is separated from each underlying dielectric-coated metal layer by a release layer.

21. The method according to claim 18, wherein the release layers are formed of an inorganic salt capable of being dissolved in an aqueous solution at room temperature.

22. The method according to claim 18, wherein the release layers are formed of NaCl, NaI, $Na_5Al_3F_{14}$, Na_3AlF_6, or $Na_2B_4O_7$.

23. The method according to claim 18, wherein the reflector layers are formed of a material selected from the group consisting of aluminum, copper, silver, gold, platinum, palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof.

24. The method according to claim 18, wherein the metal flakes have an aspect ratio of about 150 to about 500.

25. The method according to claim 18, wherein the metal flakes have a thickness of about 600 to about 1200 Å.

26. The method according to claim 18, wherein the metal flakes have a thickness of about 800 to about 1000 Å.

27. The method according to claim 18, wherein each release layer has a thickness of about 150 to about 500 Å.

28. The method according to claim 18, wherein each dielectric layer has a thickness of about 100 to about 200 Å.

29. The method according to claim 18, wherein each reflector layer has a thickness of about 400 to about 800 Å.

30. The method according to claim 18, wherein the solvent is water.

31. A method of fabricating a plurality of dielectric-coated metal flakes, comprising:

(a) forming a first release layer of $Na_2B_4O_7$ on an upper surface of a web material;

(b) forming a first dielectric-coated metal layer by:

(i) forming a bottom dielectric layer of silicon monoxide on the first release layer;

(ii) forming a reflector layer of aluminum on the bottom dielectric layer; and

(iii) forming a top dielectric layer of silicon monoxide on the reflector layer to form a first dielectric-coated metal layer on the first release layer;

(c) forming a second release layer on an upper surface of the first dielectric-coated metal layer;

(d) forming a second dielectric-coated metal layer on the second release layer;

(e) releasing the dielectric-coated metal layers from the web material and from each other by dissolving the release layers in a solvent; and

(f) fragmenting the dielectric-coated metal layers to form a plurality of dielectric-coated metal flakes.

32. The method according to claim 31, which further comprises forming a third release layer on an upper surface of the second dielectric-coated metal layer, and forming a third dielectric-coated metal layer on the third release layer.

33. The method according to claim 31, which further comprises forming a plurality of alternating release layers and dielectric-coated metal layers, the plurality of layers and layers being disposed on the second dielectric-coated metal layer and alternating such that each additional dielectric-coated metal layer is separated from each underlying dielectric-coated metal layer by a release layer.

34. The method according to claim 31, wherein the metal flakes have an aspect ratio of about 150 to about 500.

35. The method according to claim 31, wherein the metal flakes have a thickness of about 600 to about 1200 Å.

36. The method according to claim 31, wherein the metal flakes have a thickness of about 800 to about 1000 Å.

37. The method according to claim 31, wherein each release layer has a thickness of about 150 to about 500 Å.

38. The method according to claim 31, wherein each dielectric layer has a thickness of about 100 to about 200 Å.

39. The method according to claim 31, wherein each reflector layer has a thickness of about 400 to about 800 Å.

40. A thin dielectric-coated metal flake comprising:

(a) a bottom dielectric layer of silicon monoxide having a thickness of about 100 to about 200 Å;

(b) a reflector layer disposed on the bottom dielectric layer and having a thickness of about 400 to about 800 Å; and

(c) a top dielectric layer of silicon monoxide disposed on the reflector layer to form a dielectric-coated metal flake.

41. The metal flake according to claim 40, wherein the reflector layer is formed of a material selected from the group consisting of aluminum, copper, silver, gold, platinum, palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof.

42. The metal flake according to claim 40, wherein the reflector layer is formed of aluminum.

43. The metal flake according to claim 40, wherein the metal flake has an aspect ratio of about 150 to about 500.

44. The metal flake according to claim 40, wherein the metal flake has a thickness of about 600 to about 1200 Å.

45. The metal flake according to claim 40, wherein the metal flake has a thickness of about 800 to about 1000 Å.

AMENDED CLAIMS

[received by the International Bureau on 13 September 2000 (13.09.00); original claims 1, 3, 10, 18, 20, 23 and 40-42 amended; new claims 46-52 added; other claims unchanged (9 pages)]

1. A method of fabricating a plurality of dielectric-coated metal flakes, comprising:

(a) forming a first release layer on an upper surface of a web material;

(b) forming a first dielectric-coated metal layer by:

(i) forming a bottom dielectric layer on the first release layer;

(ii) forming a reflector layer on the bottom dielectric layer; and

(iii) forming a top dielectric layer on the reflector layer to form a first dielectric-coated metal layer on the first release layer;

wherein the dielectric layers are formed to have a thickness that does not substantially affect the optical properties of the reflector layer;

(c) forming a second release layer on an upper surface of the first dielectric-coated metal layer;

(d) forming a second dielectric-coated metal layer on the second release layer;

(e) releasing the dielectric-coated metal layers from the web material and from each other by dissolving the release layers in a solvent; and

(f) fragmenting the dielectric-coated metal layers to form a plurality of dielectric-coated metal flakes.

2. The method according to claim 1, which further comprises forming a third release layer on an upper surface of the second dielectric-coated metal layer, and forming a third dielectric-coated metal layer on the third release layer.

3. The method according to claim 1, which further comprises forming a plurality of alternating release layers and dielectric-coated metal layers, the plurality of layers formed on the second dielectric-coated metal layer and alternating such that each additional

dielectric-coated metal layer is separated from each underlying dielectric-coated metal layer by a release layer.

4. The method according to claim 1, wherein the release layers are formed of an inorganic salt capable of being dissolved in an aqueous solution at room temperature.

5. The method according to claim 1, wherein the release layers are formed of NaCl, NaI, $Na_5Al_3F_{14}$, Na_3AlF_6, or $Na_2B_4O_7$.

6. The method according to claim 1, wherein the dielectric layers are formed of a material having an index of refraction of about 1.65 or less.

7. The method according to claim 6, wherein the dielectric layers are formed of a material selected from the group consisting of silicon dioxide, aluminum oxide, magnesium fluoride, aluminum fluoride, cerium fluoride, lanthanum fluoride, neodymium fluoride, samarium fluoride, barium fluoride, calcium fluoride, lithium fluoride, and combinations thereof.

8. The method according to claim 1, wherein the dielectric layers are formed of a material having an index of refraction of greater than about 1.65.

9. The method according to claim 8, wherein the dielectric layers are formed of a material selected from the group consisting of zinc sulfide, zinc oxide, zirconium oxide, titanium dioxide, carbon, indium oxide, indium-tin-oxide, tantalum pentoxide, cerium oxide, yttrium oxide, europium oxide, iron oxides, hafnium nitride, hafnium carbide, hafnium oxide, lanthanum oxide, magnesium oxide, neodymium oxide, praseodymium oxide, samarium oxide, antimony trioxide, silicon carbide, silicon nitride, silicon monoxide, selenium trioxide, tin oxide, tungsten trioxide, and combinations thereof.

10. The method according to claim 1, wherein the reflector layer is formed of a material selected from the group consisting of aluminum, copper, silver, gold, platinum,

palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof.

11. The method according to claim 1, wherein the metal flakes have an aspect ratio of about 150 to about 500.

12. The method according to claim 1, wherein the metal flakes have a thickness of about 600 to about 1200 Å.

13. The method according to claim 1, wherein the metal flakes have a thickness of about 800 to about 1000 Å.

14. The method according to claim 1, wherein each release layer has a thickness of about 150 to about 500 Å.

15. The method according to claim 1, wherein each dielectric layer has a thickness of about 100 to about 200 Å.

16. The method according to claim 1, wherein each reflector layer has a thickness of about 400 to about 800 Å.

17. The method according to claim 1, wherein the solvent is water.

18. A method of fabricating a plurality of dielectric-coated metal flakes, comprising:

(a) forming a first release layer on an upper surface of a web material;

(b) forming a first dielectric-coated metal layer by:

(i) forming a bottom dielectric layer of silicon monoxide on the first release layer;

(ii) forming a reflector layer on the bottom dielectric layer; and

(iii) forming a top dielectric layer of silicon monoxide on the reflector layer to form a first dielectric-coated metal layer on the first release layer;

wherein the dielectric layers are formed to have a thickness that does not substantially affect the optical properties of the reflector layer;

(c) forming a second release layer on an upper surface of the first dielectric-coated metal layer;

(d) forming a second dielectric-coated metal layer on the second release layer;

(e) releasing the dielectric-coated metal layers from the web material and from each other by dissolving the release layers in a solvent; and

(f) fragmenting the dielectric-coated metal layers to form a plurality of dielectric-coated metal flakes.

19. The method according to claim 18, which further comprises forming a third release layer on an upper surface of the second dielectric-coated metal layer, and forming a third dielectric-coated metal layer on the third release layer.

20. The method according to claim 18, which further comprises forming a plurality of alternating release layers and dielectric-coated metal layers, the plurality of layers formed on the second dielectric-coated metal layer and alternating such that each additional dielectric-coated metal layer is separated from each underlying dielectric-coated metal layer by a release layer.

21. The method according to claim 18, wherein the release layers are formed of an inorganic salt capable of being dissolved in an aqueous solution at room temperature.

22. The method according to claim 18, wherein the release layers are formed of NaCl, NaI, $Na_5Al_3F_{14}$, Na_3AlF_6, or $Na_2B_4O_7$.

23. The method according to claim 18, wherein the reflector layer is formed of a material selected from the group consisting of aluminum, copper, silver, gold, platinum, palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof.

24. The method according to claim 18, wherein the metal flakes have an aspect ratio of about 150 to about 500.

25. The method according to claim 18, wherein the metal flakes have a thickness of about 600 to about 1200 Å.

26. The method according to claim 18, wherein the metal flakes have a thickness of about 800 to about 1000 Å.

27. The method according to claim 18, wherein each release layer has a thickness of about 150 to about 500 Å.

28. The method according to claim 18, wherein each dielectric layer has a thickness of about 100 to about 200 Å.

29. The method according to claim 18, wherein each reflector layer has a thickness of about 400 to about 800 Å.

30. The method according to claim 18, wherein the solvent is water.

31. A method of fabricating a plurality of dielectric-coated metal flakes, comprising:

(a) forming a first release layer of $Na_2B_4O_7$ on an upper surface of a web material;

(b) forming a first dielectric-coated metal layer by:

(i) forming a bottom dielectric layer of silicon monoxide on the first release layer;

(ii) forming a reflector layer of aluminum on the bottom dielectric layer; and

(iii) forming a top dielectric layer of silicon monoxide on the reflector layer to form a first dielectric-coated metal layer on the first release layer;

(c) forming a second release layer on an upper surface of the first dielectric-coated metal layer;

(d) forming a second dielectric-coated metal layer on the second release layer;

(e) releasing the dielectric-coated metal layers from the web material and from each other by dissolving the release layers in a solvent; and

(f) fragmenting the dielectric-coated metal layers to form a plurality of dielectric-coated metal flakes.

32. The method according to claim 31, which further comprises forming a third release layer on an upper surface of the second dielectric-coated metal layer, and forming a third dielectric-coated metal layer on the third release layer.

33. The method according to claim 31, which further comprises forming a plurality of alternating release layers and dielectric-coated metal layers, the plurality of layers and layers being disposed on the second dielectric-coated metal layer and alternating such that each additional dielectric-coated metal layer is separated from each underlying dielectric-coated metal layer by a release layer.

34. The method according to claim 31, wherein the metal flakes have an aspect ratio of about 150 to about 500.

35. The method according to claim 31, wherein the metal flakes have a thickness of about 600 to about 1200 Å.

36. The method according to claim 31, wherein the metal flakes have a thickness of about 800 to about 1000 Å.

37. The method according to claim 31, wherein each release layer has a thickness of about 150 to about 500 Å.

38. The method according to claim 31, wherein each dielectric layer has a thickness of about 100 to about 200 Å.

39. The method according to claim 31, wherein each reflector layer has a thickness of about 400 to about 800 Å.

40. A thin dielectric-coated metal flake comprising:

(a) a bottom dielectric layer of silicon monoxide;

(b) a reflector layer disposed on the bottom dielectric layer; and

(c) a top dielectric layer of silicon monoxide disposed on the reflector layer to form a dielectric-coated metal flake;

wherein the dielectric layers each have a thickness that does not substantially affect the optical properties of the reflector layer.

41. The metal flake according to claim 40, wherein the reflector layer comprises a material selected from the group consisting of aluminum, copper, silver, gold, platinum, palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof.

42. The metal flake according to claim 40, wherein the reflector layer comprises aluminum.

43. The metal flake according to claim 40, wherein the metal flake has an aspect ratio of about 150 to about 500.

44. The metal flake according to claim 40, wherein the metal flake has a thickness of about 600 to about 1200 Å.

45. The metal flake according to claim 40, wherein the metal flake has a thickness of about 800 to about 1000 Å.

46. A thin dielectric-coated metal flake comprising:

(a) a reflector layer having a top surface and a bottom surface, the reflector layer having a thickness of about 400 Å to about 800 Å;

(b) a first dielectric layer of silicon monoxide on the bottom surface of the reflector layer, the first dielectric layer having a thickness of about 100 Å to about 200 Å; and

(c) a second dielectric layer of silicon monoxide on the top surface of the reflector layer, the second dielectric layer having a thickness of about 100 Å to about 200 Å;

wherein the first and second dielectric layers each have a thickness that does not substantially affect the optical properties of the reflector layer.

47. The metal flake according to claim 46, wherein the reflector layer comprises a material selected from the group consisting of aluminum, copper, silver, gold, platinum, palladium, nickel, cobalt, tin, rhodium, niobium, chromium, and combinations or alloys thereof.

48. The metal flake according to claim 46, wherein the reflector layer comprises aluminum.

49. The metal flake according to claim 46, wherein the silicon monoxide of the first and second dielectric layers has a molar ratio of oxygen to silicon from about 1 to about 1.85.

50. The metal flake according to claim 46, wherein the metal flake has an aspect ratio of about 150 to about 500.

51. The metal flake according to claim 46, wherein the metal flake has a thickness of about 600 to about 1200 Å.

52. The metal flake according to claim 46, wherein the metal flake has a thickness of about 800 to about 1000 Å.

STATEMENT UNDER ARTICLE 19

Please amend the claims in the above-identified application by cancelling sheets 16 - 23 of this application which contain the claims and abstract. Please substitute therefore, sheets 16 - 24 attached hereto, which contain the new claims to be entered in this application. The abstract is identical to the abstract as originally filed and is found on substitute page 25.

The amendments submitted herein are intended to correct obvious typographical errors and place this application into conformity with the amendment entered in the corresponding U.S. application. No new matter has been introduced by these amendments. Applicants believe that the amended claims submitted herewith more accurately and distinctly point out the inventive concepts Applicant wishes to claim.

Original claims 1, 3, 10, 18, 20, 23, 40, 41 and 42 are amended by this document. Claims 46 - 52 have been added by this document.

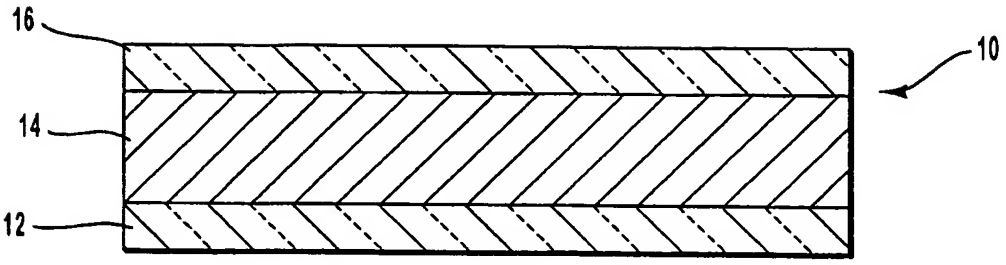

FIG. 1

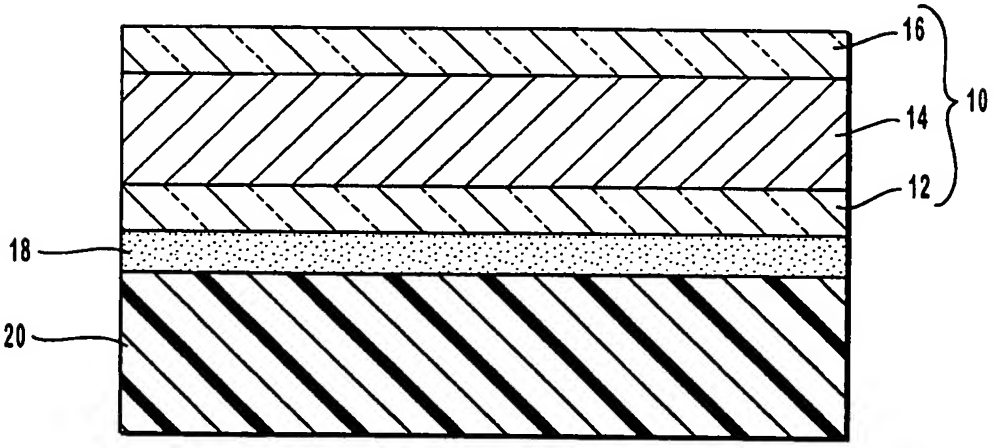

FIG. 2

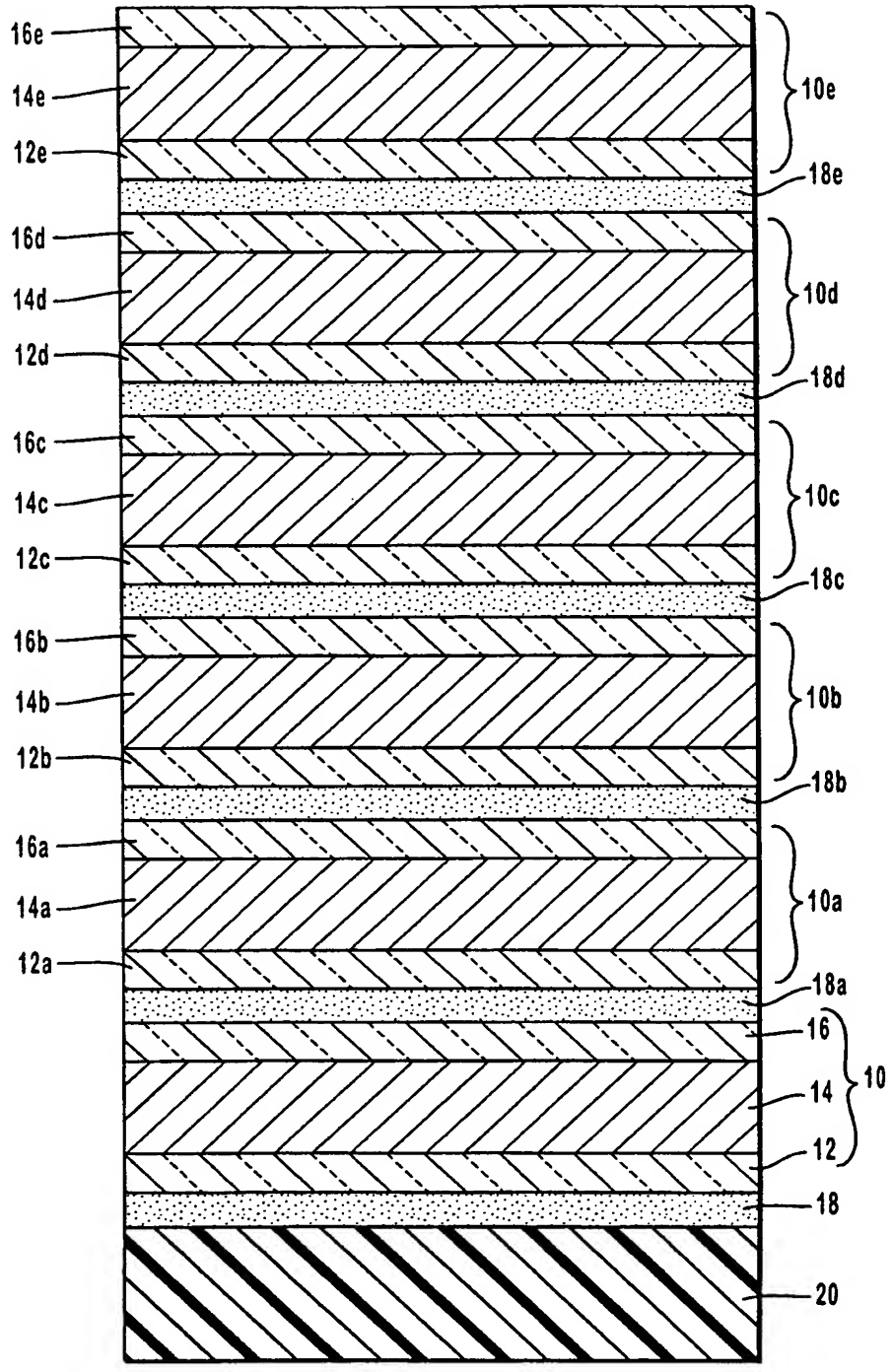
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FIG. 3

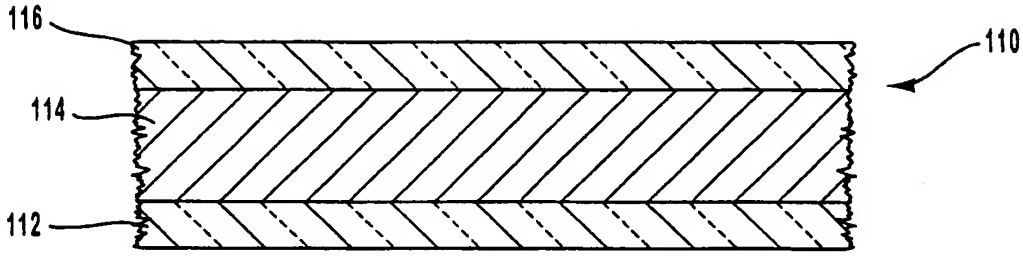
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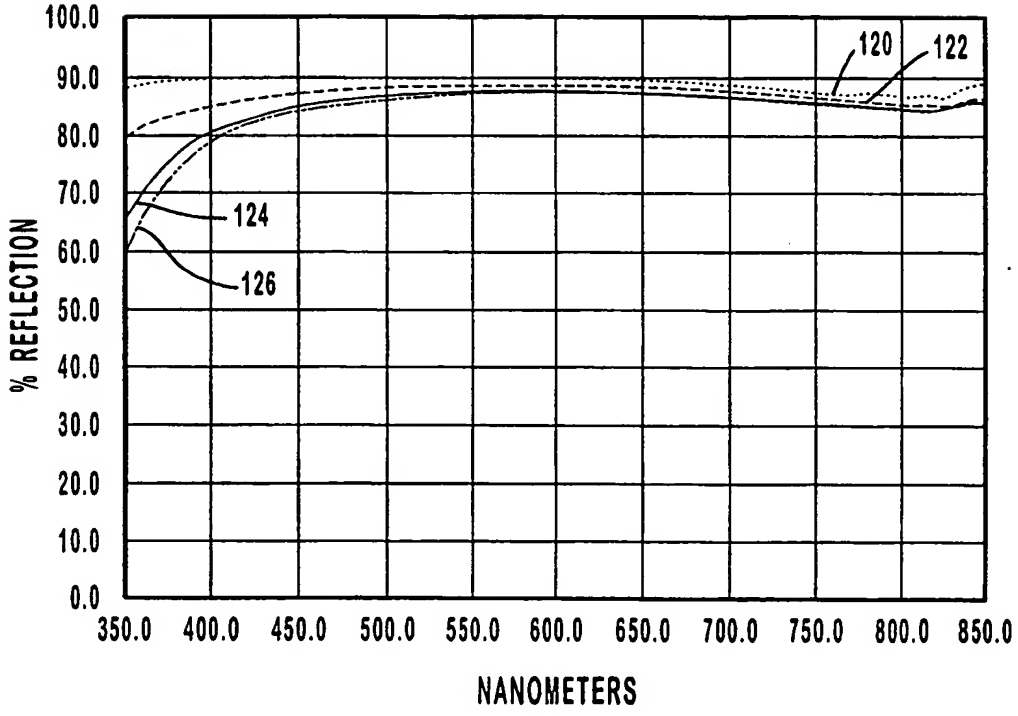
FIG. 4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850.0
NANOMETERS
120
122
124
126

FIG. 5

INTERNATIONAL SEARCH REPORT

Int .tional Ap[redacted] No
PCT/US 00/05869

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09C1/00 C09C1/64 C09C1/62 C09C3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 24946 A (AVERY DENNISON CORP ;ENLOW HOWARD H (US); JOSEPHY KARL (US); RETTK) 4 May 2000 (2000-05-04) page 4, line 1 -page 6, line 29; claims 15-17; figures 4,7	1-4, 7-10, 18-21, 23,40-45
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Y	US 5 571 624 A (COOMBS PAUL G ET AL) 5 November 1996 (1996-11-05) the whole document	1-4, 6-20, 23-30

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 July 2000	03/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Siebel, E

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INTERNATIONAL SEARCH REPORT

Int. ..tional Application No
PCT/US 00/05869

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4 434 010 A (ASH GARY S) 28 February 1984 (1984-02-28) the whole document	1-4, 6-20, 23-30

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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Information on patent family members

Int. tional Appl. n No
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Information on patent family members

Int[illegible]ional Appli[illegible]No
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